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IMPROVED SYNTHESSES OF BENZILS

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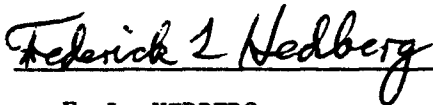
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FOR THE COMMANDER



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Three approaches were investigated to obtain a general method of synthesis of low-cost bis-benzil monomers for use in quinoxaline resin systems. Reaction of phenylmagnesium bromide with iron carbonyl and acid chlorides was unsuccessful. Reaction of acid chlorides with benzylidene triphenylphosphorane followed by periodate oxidation proved successful. Palladium catalyzed conversion of dibromoaromatics to bis-acetylenes followed by permanganate oxidation also proved successful. The scope of these reactions was explored.		

FOREWORD

This report was prepared by the University of Arizona, Tucson, Arizona under USAF Contract No. F33615-79-C-5103, Project No. FY1457-79-00846, Task No. ILIR0117. This work was administered under the direction of the Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. F. L. Hedberg (AFWAL/MLBP) as Project Scientist. This report describes work conducted from July 1979 to July 1980, and was submitted in December 1980.

The work described in this report was performed by Dr. S. Havens and Dr. C. C. Yu.

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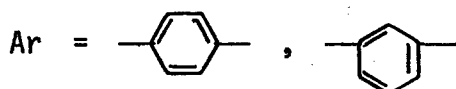
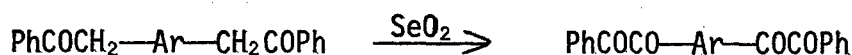
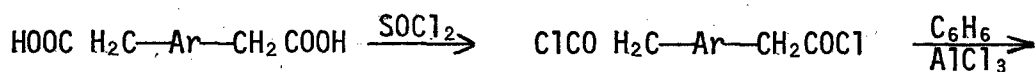
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SECTION I

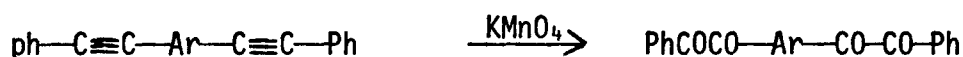
INTRODUCTION

Because of their good thermal stability, adhesive properties, durability, moisture resistance, and good processability, phenylquinoxaline polymers are currently some of the most promising materials for high temperature structural composites and adhesives. The major drawback that has hindered development of the phenylquinoxaline polymer systems has been the high cost and synthetic difficulties associated with the two types of monomers used, the tetraamines and the bis-benzils. Research efforts have substantially reduced the cost of the tetraamines during the past ten years.

Two methods, described below, were among the most developed general methods for preparation of bis-benzils. The conventional method which utilize the Friedel-Crafts reaction of aromatic bis-acetyl chlorides with benzene, followed in a subsequent oxidation with selenium dioxide¹ was a very general method for preparation of bis-benzils. This method suffers from the drawbacks of the required high-cost acid chlorides and a toxic oxidizing agent, selenium dioxide.



In the other method, a diiodoaromatic compound was treated with cuprous phenylacetylde yielding a bis-acetylene compound, which was oxidized to a bis-benzil.² This method suffers from the disadvantages of the high-cost



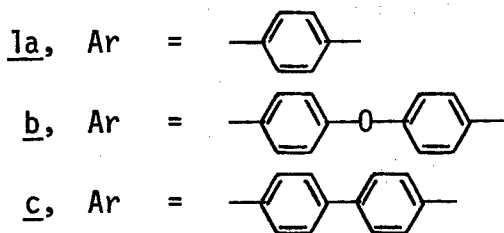
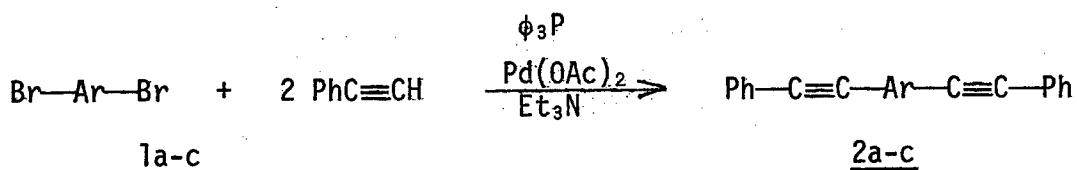
diiodoaromatic compounds and the necessity of preparation of cuprous phenylacetylide from phenylacetylene.³ We wish to report here on the results of two improved methods for preparation of bis-benzils and substituted benzils which are to be used for the study of curable polyphenylquinoxalines and acetylene terminated quinoxaline resins currently undertaken in the University of Arizona and Air Force Materials Laboratory of Wright-Patterson Air Force Base.

SECTION II

RESULTS AND DISCUSSION

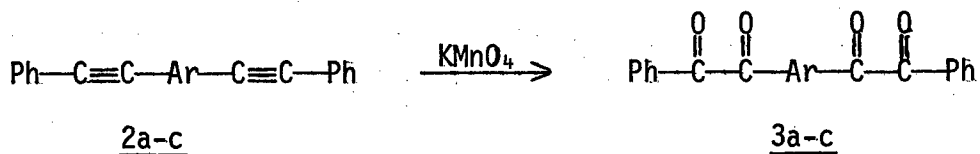
1. PREPARATION OF BIS-BENZILS BY OXIDATION OF BIS-ACETYLENES

The preparation of three bis-acetylenes was accomplished by reacting dibromoaromatic compound with phenylacetylene in the presence of palladium (II) acetate and triphenylphosphine as catalysts. The procedure for the preparation of bis-para-phenoxyphenyl-4,4'-(2,2'-diphenylethynyl)diphenyl]ketone reported earlier by P. L. Frentzel and C. S. Marvel⁴ was adopted with slight modification to prepare these three bis-acetylenes 2a-c in good yields (70-79%).



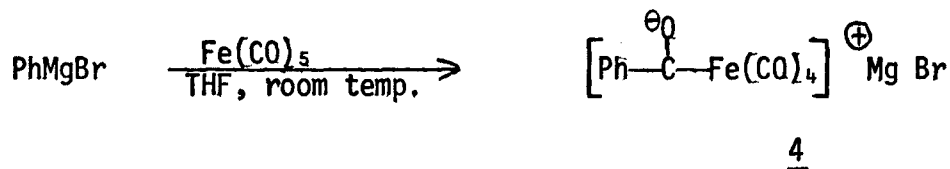
It was felt that above substitution reaction could apply to bis(p-chlorophenyl)sulfone due to the electronic withdrawing nature of sulfone group. Several attempts to prepare bis(p-phenylethynyl)diphenylsulfone met with failure possibly due to catalyst poisoning in the earlier stage.

Bis-acetylenes, 2a-c, were then oxidized with potassium permanganate, using a procedure reported by D. G. Lee and V. S. Chang,⁵ to afford bis-benzils 3a-c in very good yields (79-85%).



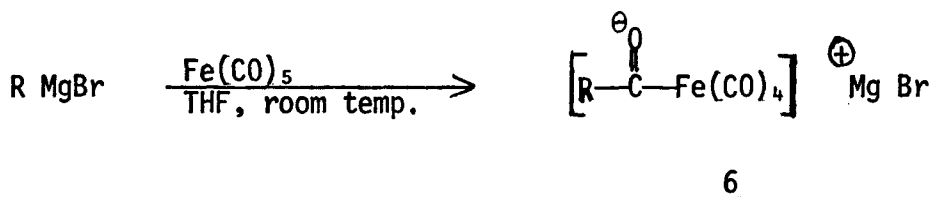
2. REACTION OF THE PHENYLMAGNESIUM BROMIDE - IRON.
PENTACARBONYL COMPLEX WITH BENZOYL CHLORIDE.

As a possible method for the synthesis of α -diketones, the reaction of the complex formed between phenylmagnesium bromide and iron pentacarbonyl with an acid chloride was investigated. This reaction was an extension



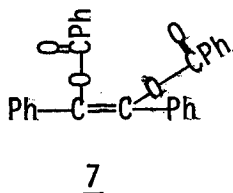
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of the reported synthesis of ketones by reaction of an acyltetracarbonylferrate, 6, with an alkyl iodide.⁶



However, an attempt to check this method by preparing acetophenone ($\text{R} = \text{Ph}$, $\text{R}' = \text{CH}_3$) was unsuccessful. Benzaldehyde was the only product isolated from the tarry reaction mixture. No trace of acetophenone was detected, although it was reported in 65% yield. It appeared that a complex did form between the Grignard reagent and iron pentacarbonyl, as evidenced by a yellow precipitate that formed when a tetrahydrofuran solution of these two reagents was cooled. The complex, 6, did not react with alkyl iodide and was decomposed to benzaldehyde upon aqueous work-up.

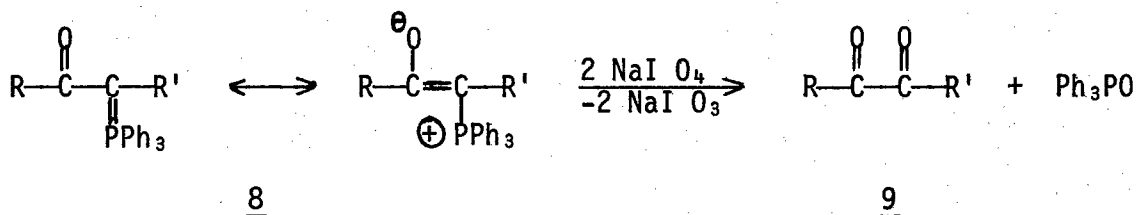
Treatment of benzoyltetracarbonylferrate, 4, with benzoyl chloride likewise failed to yield the expected benzil. The predominant product recovered from the tarry reaction mixture was again benzaldehyde. Smaller amounts of benzoic acid, biphenyl, and 1,2-dibenzoyloxystibene, 7, were also isolated. Several variations in the reaction conditions were tried.



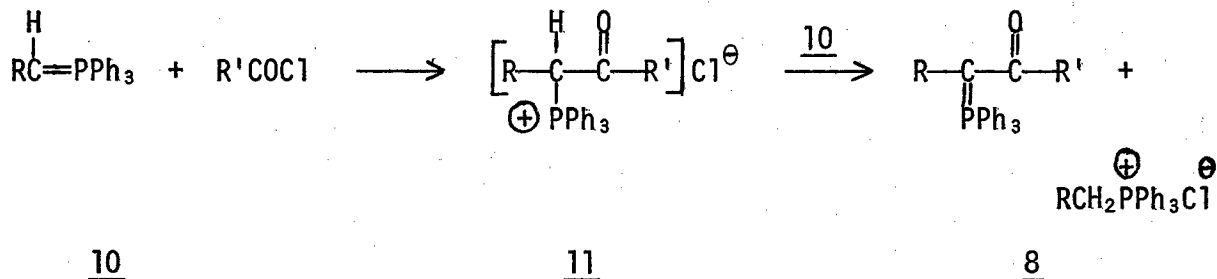
These include: (1) inverse addition - addition of the complex, 4, to a stirred solution of benzoyl chloride in tetrahydrofuran, (2), conducting the reaction in refluxing tetrahydrofuran instead of addition of benzoyl chloride to 4 at room temperature, and (3) addition of an iodine-benzoyl chloride mixture⁷ to a room temperature solution of 4. None of these variations resulted in the desired benzil.

3. PREPARATION OF BIS-BENZIL AND SUBSTITUTED BENZILS BY OXIDATION OF ACYALKYLIDENETRIPHENYLPHOSPHORANES

Bestman et al.⁸ reported that oxidation of an acylalkylidenetriphenylphosphorane, 8, by sodium meta periodate yielded the α -diketone and triphenylphosphine oxide. The acylalkylidenetriphenylphosphorane was prepared

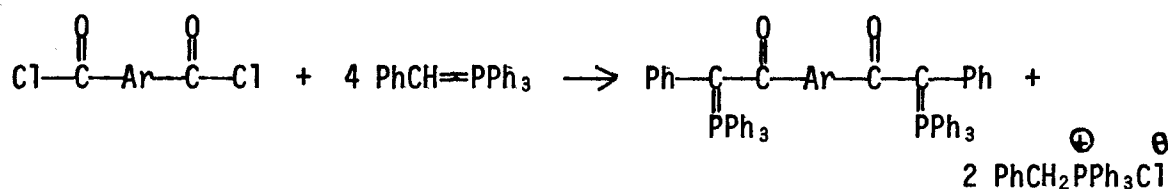


by reaction of two moles of alkylidenetriphenylphosphorane, 10, with an



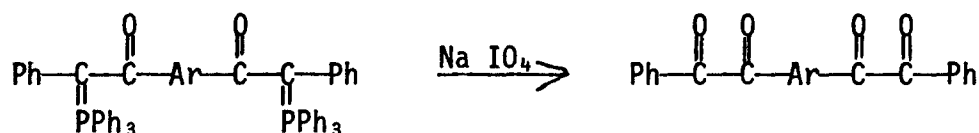
acid chloride.⁹ In this transylation, one mole of the ylide, 10, is used as a base to remove the proton from the α -carbon on the initially-formed phosphonium chloride 11. As a result, one mole of phosphonium salt is regenerated.

This general method was tried and it was found that when $R, R' = \text{Ph}$, benzil was obtained in an overall yield of 62% (starting with benzoyl chlorides). Similar procedures were used to prepare bis-benzils 14a,b, and substituted benzils 16a,b as shown below.

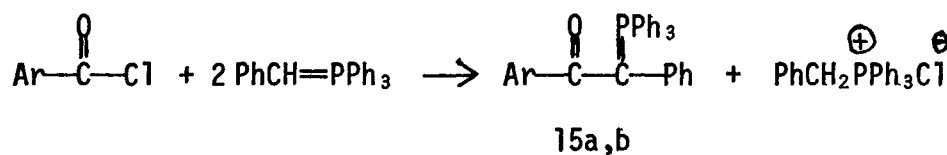
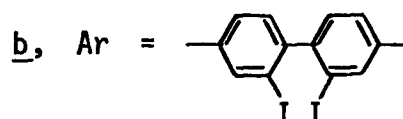
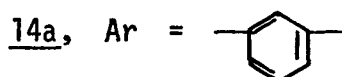


12a,b

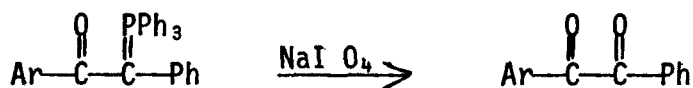
13a,b



13a,b

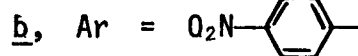
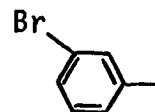


15a,b



15a,b

16a, Ar =

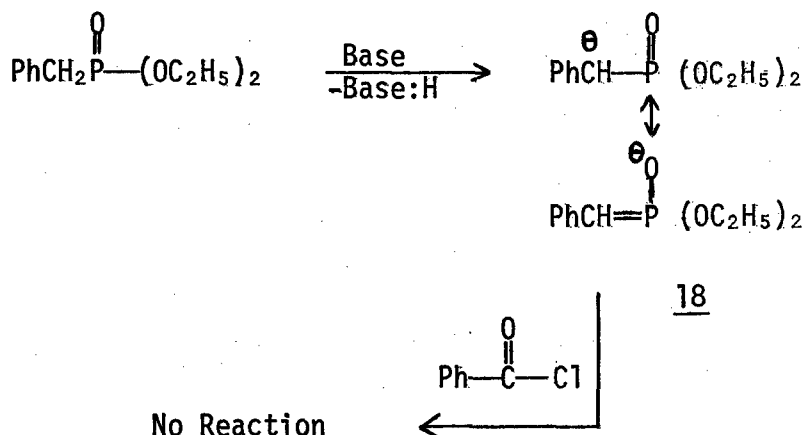


In an effort to minimize the expense of preparing these bis- α -diketones, several variations in procedure were tried. Lithium amide in benzene and potassium *t*-butoxide in dichloromethane were base-solvent combinations used instead of *n*-butyl lithium in preparation of the ylide. In neither case was the ylide effectively produced. It appears that the benzene soluble alkyl-lithiums are the only effective bases for use as long as both the formation of the ylide and the formation of 13 are carried out in benzene solution.

Other oxidants were tried in lieu of periodate. Neutral potassium permanganate¹⁰ partially oxidized 13 to 14 but much of the permanganate was lost due to autooxidation. Potassium persulfate and sodium perborate were completely ineffective. Treatment of 13 with sodium dichromate resulted in degradation to carboxylic acids. Periodate was the only effective chemical oxidant found.

The acid chloride is probably the only common carbonyl species which readily reacts with 10. The dimethyl ester of isophthalic acid failed to react with the ylide solution after several days at reflux temperature. However, the *S*-ethyl esters have been reported to react with the ylide.⁹

Another type of reactive intermediate, a phosphonate ylide,^{11,12} was prepared. It was hoped that it would react with acid chlorides in a manner analogous with 10. The possible advantages of this method were the reduced



expense of generating the ylide from diethylbenzylphosphorate and the easy removal of the oxidation by-products, which would have been water soluble phosphate esters. Generation of 18 using sodium hydride as base, followed by reacting with benzoyl chloride, resulted only in the isolation of starting materials. This method was abandoned and work continued with the phosphorane ylides.

SECTION III

EXPERIMENTAL

1. 1,4-BIS(PHENYLETHYNYL)BENZENE (2a).

p-Dibromobenzene (117.96 g, 0.500 mol), phenylacetylene (153.19 g, 1.500 mol), palladium (II) acetate (0.50 g), and triphenylphosphine (10.00 g) were dissolved in 600 ml of dry triethylamine in a 2-liter round bottom flask equipped with an overhead mechanical stirrer. The mixture was stirred and heated for 4 hr at reflux temperature under nitrogen. After cooling to room temperature, chloroform (ca. 1 liter) was added. The product mixture was filtered and the filtrate was concentrated in vacuo to yield a light brown solid. The crude solid was washed with ether (ca. 2 liter). The filtrate was concentrated in vacuo to afford 15.19 g of crude product which was recrystallized from methanol to yield 3.68 g of pure 1,4-bis(phenylethynyl)benzene (2a). The residue after ether washing was further washed with hot benzene (6 x 500 ml). The benzene solutions were combined and concentrated in vacuo to afford 88.32 g of fairly pure 1,4-bis(phenylethynyl)benzene (1a) which is pure enough for subsequent oxidation step. The total yield of 1,4-bis(phenylethynyl)benzene is 98.00 g (70.4%), m.p. 175.5-177° (lit¹³ 180-183°).

2. 1,4-BIS(PHENYLGLYOXYLOYL)BENZENE (3a)

Potassium permanganate (47.39 g, 0.300 mol) and 1,4-bis(phenylethynyl)benzene (13.92 g, 0.0500 mol) was charged into a 2-liter round bottom flask equipped with an overhead mechanical stirrer. Water (500 ml), methylene chloride (300 ml), acetic acid (25 ml) and phase-transfer agent (Adogen-464, 7.41 g) were added. The mixture was refluxed for 6 hr. After cooling to room temperature, sodium hydrogen sulfite (ca. 15 g) was added slowly to reduce any unreacted permanganate. After 15 min, the solution was acidified

with 80 ml of concentrated HCl and the precipitated manganese dioxide reduced by addition of the required amount of concentrated sodium hydrogen sulfite solution. The aqueous phase was separated, saturated with sodium chloride, and extracted with dichloromethane (3 x 200 ml). The organic layers were combined and washed with 5% aqueous sodium hydroxide solution (200 ml), dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to yield a yellow viscous liquid. The yellow liquid was dissolved in dichloromethane and recrystallized from methanol-water to afford 10.06 g (58.8%) of pure 1,4-bis(phenylglyoxaloyl)benzene as a bright yellow solid, m.p. 124-125.5° (lit.¹ 122-124°).

3. 4,4'-BIS(PHENYLETHYNYL)DIPHENYL ETHER (2b)

Bis(p-bromophenyl)ether (9.84 g, 30.0 mmol), phenylacetylene (9.19 g, 90.0 mmol), palladium (II) acetate (80 mg), and triphenylphosphine (300 mg) were dissolved in ca 12.5 g of dry triethylamine in a round bottom flask. The mixture was stirred and heated for 16 hr at reflux temperature under nitrogen. After cooling to room temperature, the crude product mixture was washed thoroughly with 4 x 50 ml ether and then by 2 x 50 ml methanol to yield an off-white solid sample of 4,4'-bis(phenylethynyl)diphenyl ether, m.p. 183-185° (lit.¹⁴ m.p. 176°); yield 8.79 g (79.2%).

4. 4,4'-BIS(PHENYLGLYOXALOYL)DIPHENYL ETHER (3b)

Potassium permanganate (71.08 g, 450.0 mmol) and 4,4'-bis(phenylethynyl)-diphenyl ether (33.30 g, 90.0 mmol) were charged into a 2-liter three neck round bottom flask equipped with an overhead mechanical stirrer. Water (ca, 400 ml), methylene chloride (400 ml), acetic acid (40 ml) and phase-transfer agent (Adogen-464; 7.0 g) were added. The mixture was refluxed for 6 hr and worked up as described earlier for the preparation of 1,4-bis(phenylglyoxaloyl)-benzene (3a). The crude yellow solid product was recrystallized from CH₂Cl₂-methanol to afford 29.54 g (75.6%) of pure 4,4'-bis(phenylglyoxaloyl)diphenyl ether, m.p. 105-106° (lit.¹⁵ 108-109°).

5. 4,4'-BIS(PHENYLETHYNYL)BIPHENYL (2c)

4,4'-dibromobiphenyl (15.60 g, 50.0 mmol), phenylacetylene (15.30 g, 150.0 mmol), palladium (II) acetate (150 mg), and triphenylphosphine (1.00 g) were dissolved in ca. 28 g of dry triethylamine in a round bottom flask. The mixture was stirred and heated for 20 hr at reflux temperature under nitrogen. After cooling to room temperature, the crude product mixture paste was washed with ca. 150 ml of ether (this ether washing solution can be concentrated and recrystallized from benzene-methanol to yield 1.09 g of crude product, m.p. 180-210°), and then with 3 x 100 ml of methanol to yield 20.02 g of a crude product. The crude product was continuously extracted with benzene using a soxhlet extractor to yield 15.11 g (84.7%) of pure 4,4'-bis(phenylethynyl)-biphenyl,^{2a} m.p. 240-243°.

6. 4,4'-BIS(PHENYLGLYOXYLOYL)BIPHENYL (3c)

Potassium permanganate (71.08 g, 450.0 mmol) and 4,4'-bis(phenylethynyl)-biphenyl (31.86 g, 90.0 mmol) were charged into a 2-liter three neck round bottom flask equipped with an overhead mechanical stirrer. Water (ca. 400 ml), methylene chloride (400 ml), acetic acid (40 ml) and phase-transfer agent (Adogen-464; 5.3 g) was added. The mixture was refluxed for 6 hr. After cooling, sodium bisulfite solution was added to reduce any unreacted permanganate. After 15 min, the solution was acidified with ca. 100 ml of conc. HCl and the precipitated manganate dioxide reduced by addition of required amount of concentrated sodium bisulfite solution. The product solution mixture was filtered to yield yellow crude solid. The organic phase of filtrate was concentrated in vacuo to afford more crude yellow solid. The crude yellow solids were combined, washed thoroughly with distilled water, dried, and recrystallized from CHCl₃-MeOH to afford 30.71 g (81.6%) of pure 4,4'-bis(phenylglyoxaloyl)biphenyl, m.p. 202-204° (lit.¹⁶ 205-206°).

7. BENZYLTRIPHENYLPHOSPHONIUM CHLORIDE

Benzyl chloride, 139.3 g (1.10 mole) was added to 262.3 g (1.00 mole) of triphenylphosphine in a 2-L Erlenmeyer flask. Solution occurred after the stirred mixture was heated on a hot plate for several minutes. The salt started to precipitate after 20 - 30 min. Heating was continued until a solid mass formed. The solid was pulverized, washed thoroughly with several portions of benzene, and collected by filtration. It was then dried under vacuum at 80°C for 6 hr, m.p. 332.5-335.5° (lit. ¹⁷ 317-318°). Yields ranged from 90-95%.

8. 1,3-BIS(CARBONYLBENZYLIDENETRIPHENYLPHOSPHORANE)BENZENE (13a)

n-Butyllithium (0.4 mole) was injected by syringe into a 2-L three-necked flask containing a mechanically stirred suspension of 155.6 g (0.4 mole) of benzyltriphenylphosphonium chloride in 400 mL of dry benzene under a nitrogen atmosphere. The bright red-orange suspension was stirred at room temperature for 1 hr and then heated to reflux. Isophthaloyl chloride, 20.3 g (0.1 mole) dissolved in 100 mL of benzene was added to the refluxing benzylidenetriphenylphosphorane solution over a 2 hr period. The solvent was evaporated and residual solvent removed from the solid under vacuum at 80°. The material was then stirred with water, filtered, and washed with water to remove the benzyltriphenylphosphonium chloride. The crude 1,3-bis(carbonylbenzylidenetriphenylphosphorane)benzene was dried under vacuum at 80° for 6 hr. This material was oxidized without further purification to 1,3-bis(phenylglyoxaloyl)benzene. Recrystallization from benzene afforded an analytical sample, m.p. 243-244°.

Analysis Calc'd for C₅₈ H₄₄ O₂ P₂: C, 83.44; H, 5.31; P, 7.42.

Found: C, 83.06; H, 5.16; P, 7.18

9. 1,3-BIS(PHENYLGLYOXALOYL)BENZENE (14a)

The crude 1,3-bis(carbonylbenzylidenetriphenylphosphorane)benzene (13a) was placed in a 1-L round-bottomed flask and a suspension of 101.2 g (0.44 mole) of potassium meta periodate in 500 mL of water added. The mixture was stirred at reflux temperature for 3 hr, cooled, and extracted with four 100 mL portions of ether. The combined ethereal extracts were dried over anhydrous magnesium sulfate, which was removed by filtration. The ether was evaporated to leave a yellow oil which was crystallized from approximately 150-200 mL of ethanol. Crude 1,3-bis(phenylglyoxaloyl)benzene (14a), 24.2 g, was collected by filtration and recrystallized from 300 mL of ethanol to yield 18.1 g (53%) of pure material, m.p. 96.5-98° (lit.¹⁸ 98-99.5°).

10. 4,4-BIS(CARBONYLBENZYLIDENETRIPHENYLPHOSPHORANE)-2,2'-DIIODODIPHENYL (13b)

n-Butyllithium (0.2 mole) was injected by syringe into a 1-L three-necked flask containing a mechanically stirred suspension of 77.8 g (0.2 mole) of benzyltriphenylphosphonium chloride in 200 mL of dry benzene under a nitrogen atmosphere. The bright red-orange suspension was stirred at room temperature for 1 hr and then heated to reflux. 4,4'-Dichloroformyl-2,2'-diiododiphenyl¹⁹ 26.55 g (0.05 mole) dissolved in 100 mL of benzene was added to the refluxing benzylidenetriphenylphosphorane solution over a 2 hr period. The solvent was evaporated and residual solvent removed from the solid under vacuum at 80°. The material was then stirred with water, filtered, and washed with water to remove the benzyltriphenylphosphonium chloride. The crude 4,4'-bis(carbonylbenzylidenetriphenylphosphorane)-2,2'-diiododiphenyl was dried under vacuum at 80° for 6 hr. This material was oxidized without further purification to 4,4'-bis(phenylglyoxaloyl)-2,2'-diiododiphenyl (13b). Recrystallization from benzene afforded an analytical sample, m.p. 235.5-236.5°.

Analysis Calc'd for C ₆₄ H ₄₆ I ₂ O ₂ P ₂ :	C, 66.11; H, 3.99; I, 21.83; P, 5.33.
Found:	C, 67.87; H, 4.16; I, 20.66; P, 4.84.

11. 4,4'-BIS(PHENYLGLYOXYLOYL)-2,2'-DIIODODIPHENYL (14b)

The crude 4,4'-bis(carbonylbenzylidene-triphenylphosphorane)-2,2'-diiododiphenyl (0.05 mole) was dissolved with warming in 200 mL of pyridine. The stirred solution was heated to reflux and a solution of 47.1 g (0.22 mole) of sodium meta periodate in 300 mL of water slowly added to the refluxing solution over a period of 2 hr. The suspension was stirred at reflux for an additional 3 hr. Most of the solvent was evaporated and the aqueous residue extracted with four 100 mL portions of ether. The combined ethereal extracts were washed with dilute hydrochloric acid and with water. The ether was dried over anhydrous magnesium sulfate, which was removed by filtration, and evaporated to a volume of approximately 150 mL. The triphenylphosphine oxide, which precipitated after cooling overnight in a refrigeration, was removed by filtration. The filtrate was evaporated to leave a yellow oil. Crystallization was effected by boiling the oily residue in 100 mL of ethanol.²⁰ After setting for several days, 17.4 g of crude 4,4'-bis(phenylglyoxaloyl)-2,2'-diiododiphenyl (14b) was collected by filtration. Recrystallization from ethanol-chloroform gave 14.8 g of pure material, m.p. 143-144°, in 44% yield.

Analysis Calc'd for C₂₈ H₁₆ I₂ O₄: C, 50.18; H, 2.41; I, 37.87.

Found: C, 50.07; H, 2.33; I, 37.68.

12. m-BROMOBENZOYLBENZYLIDENETRIPHENYLPHOSPHORANE (15a)

A three-necked round-bottom flask equipped with a mechanical stirrer was charged with 77.8 g (0.2 mol) of benzyltriphenylphosphonium chloride in 200 ml of dry benzene. Upon stirring and under a nitrogen atmosphere, n-butyllithium (125 ml of 1.6 M n-butyllithium in hexane, 0.2 mol) was injected via a syringe into the stirring suspension of phosphonium salt. The bright orange-red suspension was stirred at room temperature for a few minutes and heated to reflux temperature in a hour. m-Bromobenzoyl chloride (21.95 g, 0.1 mol) was added to the refluxing benzylidenetriphenylphosphorane solution over an 1 hr period. The resulting yellow suspension was filtered

to yield a yellow solid. The filtrate was concentrated and water was added to the concentrated residue. The residue was filtered and washed with more distilled water. The crude yellow solid (66.79 g) of 15a was obtained after drying in a vacuum oven overnight.

13. m-BROMOBENZIL (16a)

The crude m-bromobenzoylbenzylidenetriphenylphosphorane (15a) (0.1 mol) was added to a warm solution of 48.63 g (0.227 mol) of sodium periodate in 250 ml water in a three-necked round-bottom flask equipped with a mechanical stirrer. The suspension was heated to reflux and stirred vigorously for 3 hr. The resulting reaction mixture was extracted with methylene chloride. The extracts were dried (MgSO_4), filtered, and concentrated in vacuo to yield a yellow oil which was then recrystallized from ethanol to afford a crude solid m-bromobenzil. The crude solid was washed with hot heptane and filtered. The filtrate was recrystallized from heptane to yield 13.78 g (48.2%) of pure m-bromobenzil, m.p. $80.5\text{--}81.5^\circ$, as a bright yellow solid.

14. p-NITROBENZOYLBENZYLIDENETRIPHENYLPHOSPHORANE (15b)

A three-necked round-bottom flask equipped with a mechanical stirrer was charged with 233.4 g (0.6 mol) of benzyltriphenylphosphonium chloride in 500 ml of dry benzene. Upon stirring and under a nitrogen atmosphere, n-butyllithium (375 ml of 1.6 M n-butyllithium in hexane, 0.6 mol) was added dropwise into the stirring suspension of phosphonium salt in half an hour. p-Nitrobenzoyl chloride (55.67 g, 0.3 mol) was added to the refluxing benzylidenetriphenylphosphorane solution over a 2 hr period. The resulting orange suspension was filtered to afford 172.80 g of orange-colored crude p-nitrobenzoylbenzylidenetriphenylphosphorane (15b) after drying in a vacuum oven overnight.

15. p-NITROBENZIL (16b)

The crude p-nitrobenzoylbenzylidenetriphenylphosphorane (15b) (0.2 mol) was charged into a three-necked round-bottom flask equipped with a mechanical stirrer. Water (200 ml) was added into it and the suspension was heated to reflux temperature. A hot solution of 94.12 g (0.44 mol) of sodium periodate in 250 ml of water was added into the stirred suspension of (15b) in 1 hr. The reaction mixture was refluxed for another hour. The resulting reaction mixture was extracted with methylene chloride. The extracts were dried (MgSO_4), filtered, and concentrated in vacuo to afford a crude solid of (16b). After recrystallization twice from ethanol, pure p-nitrobenzil (30.14 g, 59.0%) was obtained as a bright yellow solid, m.p. 139-140^o (lit.²¹ 142^o).

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